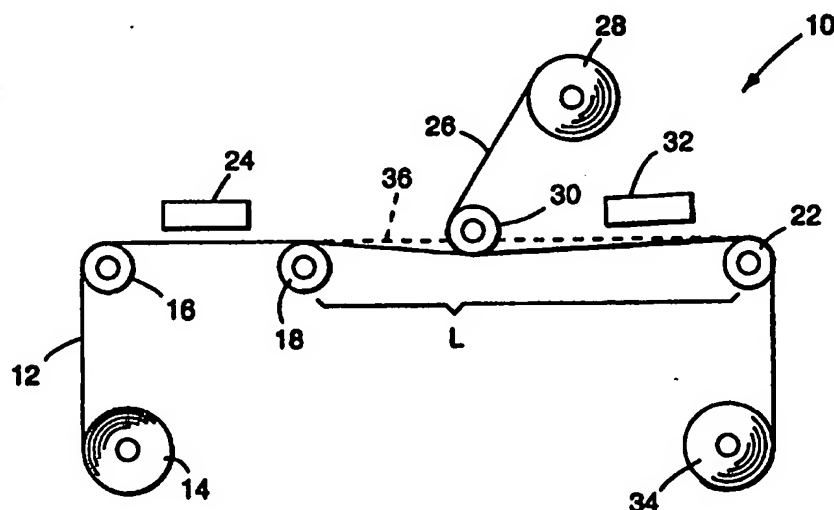


PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 31/06	A1	(11) International Publication Number: WO 97/10103 (43) International Publication Date: 20 March 1997 (20.03.97)
<p>(21) International Application Number: PCT/US96/13177</p> <p>(22) International Filing Date: 14 August 1996 (14.08.96)</p> <p>(30) Priority Data: 08/527,141 12 September 1995 (12.09.95) US</p> <p>(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(72) Inventors: VESLEY, George, F.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LEONARD, William, K.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). WILLIE, Bradley, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(74) Agents: SPRAGUE, Robert, W. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p>	<p>(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	

(54) Title: LAMINATION PROCESS FOR COATINGS



(57) Abstract

A method of preparing a laminate that includes the steps of (a) introducing a first substrate (26) having first and second surfaces and supported at two or more points into a lamination zone (L) located between two of the support points (the first substrate being unsupported throughout the lamination zone); and (b) introducing a second substrate (12) having first and second surfaces into the lamination zone (the second substrate passing around a lamination bar (30) to position the first surfaces of the substrates in a facing relationship with each other). At least one of the first surfaces is provided with coating which is most preferably a solvent-free polymerization coating. Next, in step (c), the lamination bar (30) is depressed to laminate the second substrate to the first substrate.

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

WO 97/10103

PCT/US96/13177

-1-

LAMINATION PROCESS FOR COATINGS

Background of the Invention

5 Field of the Invention

This invention relates to preparing laminates in which a coating is sandwiched between two substrates.

Description of the Related Art

10 Laminated structures in which a polymerizable coating is sandwiched between two substrates are known.

It is desirable to maintain the thickness of a coating laid down on the substrates during lamination. It is further desirable to avoid air entrainment during lamination; such entrainment causes bubbles to develop
15 in the laminate structure. In addition, during construction of multi-layer structures, it is desirable to minimize inter-layer mixing.

Summary of the Invention

20 In general, the invention features a method of preparing a laminate that includes introducing a first substrate having first and second surfaces and supported at two or more points into a lamination zone located between two of the support points. The first substrate is unsupported throughout the lamination
25 zone. A second substrate, also having first and second surfaces, is introduced into the lamination zone as well. The second substrate passes around a lamination bar to position the first surfaces of the two substrates in a facing relationship with each other.
30 At least one of the first surfaces is provided with a coating. The lamination bar is depressed to laminate the second substrate to the first substrate.

WO 97/10103

PCT/US96/13177

-2-

In preferred embodiments, the thickness of each of the substrates is no greater than about 0.635 mm (25 mils). The total thickness of the coating preferably ranges from about 0.0635 mm (0.25 mils) to about 6.35 mm (250 mils). One or both of the substrates may be provided in the form of a continuous belt. Following coating, the substrate can be delaminated and re-used. Moreover, a first surface of each substrate may be provided with a coating.

The lamination bar may be a solid bar or a hollow tube. In the case of the latter, the tube may be an air-pressurized lamination tube adapted to create a cushion of air between the second substrate and the tube. The lamination bar is preferably adjusted to depress the first substrate about 0.25 to about 12.7 mm (10 to about 500 mils), preferably about 1.27 - 3.8 mm (50-150 mils), relative to the plane defined by the first substrate and the two support points.

In certain preferred embodiments of the invention, the coating applied to at least one of the first surfaces is polymerizable. In other preferred embodiments, the coating is substantially solvent-free (i.e., at least about 80% solids) and is more preferably essentially solvent-free. In certain most preferred embodiments, the coating is polymerizable and solvent-free.

Examples of preferred polymerizable coatings include (a) a mixture of liquid crystal and polymerizable matrix reactants which upon polymerization yields a polymer dispersed liquid crystal film and (b) reactants which upon polymerization yield an adhesive, e.g., a pressure sensitive adhesive.

WO 97/10103

PCT/US96/13177

-3-

The invention allows gentle placement of a substrate onto the coated surface of another substrate, thereby minimizing air entrainment at the point of lamination and thus minimizing bubble or pinhole formation. The invention thus provides laminates having a uniform polymerizable coating sandwiched between two thin flexible substrates (one or both of which may be subsequently removed). The thickness of the coating (which is established prior to lamination when the coating is applied to one or both of the substrates) is not disturbed during the lamination process. The invention is particularly useful in the preparation of optical quality films such as polymer dispersed liquid crystal films in which the optical properties of the device are sensitive to irregularities such as thickness variations in the optically responsive film. The invention is also useful in the preparation of various adhesive constructions, e.g., optical adhesives, transfer tapes, foam-like adhesives, and cellular pressure sensitive adhesive membranes, as well as heat-activated films, vibration damping materials, protective coatings, and thin films. The invention is useful as well in the preparation of "wet-on-wet" constructions involving application of two or more polymerizable coatings because inter-layer mixing is minimized.

Other features and advantages of the invention will be apparent from the following description of the preferred embodiments thereof, and from the claims.

Brief Description of the Drawings

The invention will be more fully understood with reference to the following drawings in which:

WO 97/10103

PCT/US96/13177

-4-

Fig. 1 is a schematic drawing showing steps in the lamination process according to the invention.

Fig. 2 is a schematic drawing showing steps in the lamination process according to the invention,
5 including multiple coating operations.

Fig. 3 is a schematic drawing showing steps in the lamination process according to the invention,
including multiple lamination operations.

Fig. 4 is a schematic drawing showing steps in the lamination process according to the invention in which
10 one of the substrates is provided in the form of a continuous belt.

Fig. 5 is a cross-sectional view of an extrusion die useful in preparing laminates according to the
15 invention.

Fig. 6 is an enlarged cross-sectional view of the die of Fig. 5.

Fig. 7 is a cross-sectional view of an alternative configuration for a die useful in preparing laminates
20 according to the invention.

Description of the Preferred Embodiments

Referring to Fig. 1, there is shown a lamination apparatus 10 for preparing laminates in which, for example, an essentially solvent-free (i.e., 100% solids) polymerizable coating is sandwiched between two
25 flexible substrates 12, 26. As shown in Fig. 1, a first thin flexible substrate 12 (typically having a thickness no greater than about 0.64 mm (25 mils)) is dispensed from an unwind roll 14. Examples of suitable materials for substrate 12 include polymeric films such as polyesters (e.g., polyethylene terephthalate),
30 polyethersulfones, polyimides, and polycarbonates. In the case of devices for optical applications (e.g.,

WO 97/10103

PCT/US96/13177

-5-

light modulating devices), substrate 12 preferably is transparent. Substrate 12 may also include an electrically conductive material, e.g., chromium, indium tin oxide, tin oxide, stainless steel, gold, silver, copper, aluminum, titanium, cadmium stannate, transition metal oxides, and mixtures and alloys thereof, to enable substrate 12 to function as an electrode.

Substrate 12 is supported, for example, by a series of three intermediate rolls 16, 18, and 22. Roll 18 may be a driven backup if a die coating method is used while roll 22 may be an idler roll. The area between rolls 18 and 22 defines a lamination zone L. Substrate 12 is unsupported throughout the lamination zone.

Before entering the lamination zone, substrate 12 is provided with an essentially solvent-free polymerizable coating which is deposited at a coating station 24. Any type of polymerizable coating may be deposited. Examples include mixtures of liquid crystal and polymerizable matrix reactants which, upon exposure to ultraviolet radiation, polymerize to form an optically responsive PDLC film in which liquid crystal is dispersed throughout a polymer matrix. Examples of suitable matrix reactants include mono-functional (i.e., having one polymerizable group) and multi-functional (i.e., having two or more polymerizable groups) reactants such as mono- and multi-functional enes (i.e., an "ene" is a reactant having a polymerizable carbon-carbon double bond; e.g., acrylates, methacrylates, acrylamides, methacrylamides, vinyl silanes, allyls, and vinyl ethers); thiols;

WO 97/10103

PCT/US96/13177

-6-

silicon hydrides; alcohols; epoxies; isocyanates; amines; and/or combinations thereof.

Also suitable are reactants which upon polymerization yield adhesives, e.g., pressure sensitive adhesives, foam-like adhesives, and cellular pressure sensitive adhesive membranes. The reactants may be thermally or radiation cured. Examples include alkyl acrylates and methacrylates, epoxies, isocyanates, and combinations thereof.

Also suitable are reactants which upon polymerization yield films or protective coatings (e.g., acrylates, epoxies, vinyl ethers, and combinations thereof), as well as reactants that yield vibration damping materials (e.g., acrylates). The reactants may be thermally or radiation cured.

The polymerizable coating may be deposited on substrate 12 at coating station 24 by a wide variety of coating techniques. Examples include knife coating, reverse roll coating, notched bar coating, gravure coating, slide coating, curtain coating, spray coating, extrusion coating, and other conventional coating techniques. Where caliper control of the polymerizable coating is important (e.g., in the preparation of optical quality films), a precision coating die may be used such as described in Vesley et al., WO 95/29766, entitled "Precision Coating Process for Preparing Polymerizable Films" filed concurrently with, and assigned to the same assignee as the present application.

Once substrate 12 has been coated with the polymerizable coating, it is transported from coating station 24 into the lamination zone located between idler rolls 18 and 22. A second substrate 26 (which

WO 97/10103

PCT/US96/13177

-7-

may be the same material as substrate 12) is dispensed from an unwind roll 28 into the lamination zone as well. Substrate 26 passes around a lamination bar 30, causing the direction of the moving substrate to change.

Lamination bar 30 is preferably an air-pressurized, sintered metal, hollow tube typically measuring 2.54 - 10.16 cm (1-4 inches) in diameter; the air pressure delivered to bar 30 (typically about 1.4 - 4.5 bar) allows substrate 26 to ride on a cushion of air as it passes around lamination bar 30. Lamination bar 30 may also be in the form of a hollow tube provided with slots or holes; such tubes are particularly useful in the case of substrates requiring relatively large turning radii. Bar 30 may also be in the form of an idler roll (which may be solid or hollow), or in the form of a solid or hollow cylinder that serves as a turning point for the substrate. Preferably, bar 30 is close to roll 18.

Lamination is accomplished by mechanically depressing bar 30, thereby causing deflection of substrate 12 below the plane indicated by dotted line 36 that it would normally follow as it passed between rolls 18 and 22. The extent of deflection is referred to as "interference." The interference is generally in the range of about 0.64 - 6.35 mm (25-250 mils), and preferably in the range 1.27 - 3.8 mm (50-150 mils). The particular value for the interference is chosen based upon the viscosity and fluid properties of the polymerizable coating, web speed, and caliper of the substrate. If the interference is not sufficiently high, air entrainment may occur, resulting in pinhole formation in the polymerized coating. On the other

WO 97/10103

PCT/US96/13177

-8-

hand, excessive interference can cause spreading of the polymerizable coating, thereby reducing coating thickness.

5 Following lamination, the resulting unpolymerized sandwich is transported to a reaction station 32 where it is exposed, e.g., to heat, ultraviolet radiation, visible radiation, or a combination thereof, as is well-known in the art, to polymerize the coating. Reaction station 32 preferably is located in close
10 proximity to the coating zone and may encompass idler roll 22. Preferably, the coating should be at least partially polymerized before reaching roll 22 to prevent disturbing the caliper of the coating. The resulting laminate may then be wound onto take-up roll
15 34.

 Referring to Fig. 2, multiple coatings may be applied using several coating stations 24 and 40; additional coating stations may be included as well. The advantage of the present lamination in applying
20 multiple coatings is that inter-layer mixing of the uncured coatings is minimized.

 Referring to Fig. 3, more than two substrates may be laminated together through the inclusion of multiple lamination zones. As shown in Fig. 3, the laminate
25 formed from substrates 12 and 26 is passed to a reaction station 54 to polymerize the polymerizable coating; alternatively, reaction station 54 may be eliminated and a single reaction station 32 used to polymerize all coatings. Next, a third substrate 48
30 dispensed from an unwind roll 50 is provided with a polymerizable coating at coating station 56 and then laminated to substrate 26 in the lamination zone defined by idler rolls 42 and 22 by means of lamination

WO 97/10103

PCT/US96/13177

-9-

roll 52. The multiple lamination zone embodiment shown in Fig. 3 may be combined with multiple coating stations (as shown in Fig. 2) as well.

5 It may be desirable for one or both of the substrates to be removable. In one embodiment, the removable substrate may be dispensed in the form of a continuous belt as shown in Fig. 4. The lamination apparatus 60 shown in Fig. 4 is identical to the apparatus shown in Fig. 1 except that first substrate
10 62 is provided in the form of a continuous belt supported by idler rolls 16, 18, 22, 64 and 66. The coatable surface of substrate 62 may be provided with a release coating if desired. Following lamination and polymerization of the coating, substrate 62 is
15 delaminated from substrate 26 and then re-used in the lamination process. Substrate 26 (which now contains the polymerized coating is then passed around idler roll 68 and wound onto take-up roll 34. Multiple coating stations and/or lamination zones may be used in
20 conjunction with the continuous belt embodiment as well.

It is understood that alternative arrangements of support rolls and the lamination bar other than those illustrated above fall within the scope of this
25 invention. For example, configurations with the support rolls positioned above the substrate and the lamination bar positioned below the substrate or the support rolls positioned on one side of a vertical substrate and the lamination bar positioned on the
30 opposite side of the substrate will exhibit comparable performance to the configurations described above.

WO 97/10103

PCT/US96/13177

-10-

The invention will be more fully understood with references to the following examples which are not to be construed as limiting the scope of the invention.

EXAMPLES

5 In all of the Examples, coating was carried out by pumping an unpolymerized fluid of polymerizable reactant(s) (and additives such as liquid crystal, if present) to a coating die through which the fluid was extruded onto the electrode side of a substrate
10 according to the process described in greater detail in Vesley et al., WO 95/29766, entitled "Precision Coating Process for Preparing Polymerizable Films" filed concurrently with, and assigned to the same assignee as the present application.

15 The coating die 140 is shown in Figure 5. The unpolymerized fluid 144 was supplied by a pump 146 to the die 140 for application in the form of a continuous coating bead to the moving substrate 148, supported by a backup roll 150. Where indicated in the examples,
20 vacuum chamber 142 applied vacuum upstream of the bead to stabilize the coating bead. The unpolymerized fluid 144 was supplied through a channel 152 to a manifold 154 for distribution through a slot 156 and coating onto the moving substrate 148. The height of slot 156
25 was controlled by means of a U-shaped shim 141 (typically made of brass or stainless steel).

Referring to Figure 6, die 140 consisted of an upstream bar 164 and a downstream bar 166. The lip of the upstream bar was formed as a curved land 168 and
30 the lip of the downstream bar was formed as a substantially straight sharp edge 170 having an edge radius no greater than 10 microns. The radius of the curved land 168 was equal to the radius of the backup

WO 97/10103

PCT/US96/13177

-11-

roll 150 plus a minimal, and non-critical, 0.13 mm allowance for coating gap and film thickness.

5 The length L_1 of the curved land 168 on the upstream bar 164 was 12.7 mm. The edge angle A_1 of the downstream bar 166 is 30-60; more preferably 50-60°. The die attack angle A_2 between the downstream bar 166 surface of the coating slot 156 and the tangent plane P through a line on the film 148 surface parallel to, and directly opposite, the sharp edge 170 was either 90 or
10 95°.

The coating gap G_1 is the distance between the sharp edge 170 and the film 148. Slot height H is the distance between upstream bar 164 and downstream bar 166, and was controlled by controlling the thickness of
15 shim 141. The slot height used in the examples was 152 microns. Overbite O is a positioning of the sharp edge 170 of the downstream bar 166, with respect to the downstream edge 172 of the curved land 168 on the upstream bar 164, in a direction toward the film 148.

20 Convergence C is a counterclockwise, as shown in Fig. 6, positioning of the curved land 168 away from a location parallel to the film 148, with the downstream edge 172 being the center of rotation. In the examples, convergence was 0 or 0.57°.

25 Fig. 7 shows an alternate configuration of the die where the vacuum bar 174 is isolated from the bottom die bar 65 by a flexible metal seal 188. This configuration allows adjustment of the coating gap G_1 and convergence C without affecting the vacuum land gap
30 G_2 .

The width of the coating produced by a given die was reduced where indicated by "deckling" the die and the vacuum chamber by concurrently incorporating a)

WO 97/10103

PCT/US96/13177

-12-

shaped plugs to reduce the widths of the die cavity manifold 154 and vacuum chamber 142 to the deckling width and b) a shim into the die that has a shim slot width corresponding to the deckling width.

5

Test Procedure A

The electro-optical responses of the PDLC devices were characterized using a computer-controlled test stand consisting of an IBM personal computer interfaced with Kepco 125-1KVA-3T power supply, a Dyn-Optics Optical Monitor 590, and a Valhalla Scientific 2300 Series Digital Power Analyzer. The optics of the Dyn-Optics Optical Monitor were adjusted such that the specular transmission of photopically-filter light at an approximate 6° collection half angle was measured relative to an open beam.

15

A sample of a PDLC film/electrode sandwich measuring several square centimeters was attached to the leads of the power supply using a connector such as that described in the aforementioned Engfer et al. application. A 60 Hz voltage ranging from zero to 120 volts AC (VAC) was applied to the sample in 5 VAC increments and the specular transmission recorded.

20

Test Procedure B

The haze of the powered (120 VAC, 60 Hz) PDLC devices was measured using a Pacific Scientific Gardner XL-835 Colorimeter according to the manufacturer's instructions.

25

Examples 1-2

Two adhesive compositions were prepared from prepolymer syrups consisting of a mixture of 90 wt.% iso-octyl acrylate and 10 wt.% acrylic acid (Aldrich, Milwaukee, WI) containing 0.04 wt.% photoinitiator 2-phenyl-2,2-dimethoxy acetophenone (KB-1, Sartomer, West

30

WO 97/10103

PCT/US96/13177

-13-

Chester, PA) as described in U.S. Pat. No. 4,330,590 (Vesley). The syrups were partially photopolymerized to viscosities of 360, and 5600 cps (as measured on a Brookfield viscometer using a #4 spindle operating at 5 60 rpm) by varying the exposure times.

After the syrups had been advanced to the indicated viscosities, an additional 0.1 wt.% KB-1 photoinitiator and 0.2 wt.% hexanediol diacrylate (Sartomer, West Chester, PA) were added to the syrups 10 and the mixtures agitated until homogeneous fluids were obtained. The resulting fluids were coated on the substrates at the thicknesses indicated in Table 1 using a precision coating die as described above.

During the coating operation, the first substrate 15 was unwound from a first unwind roll and passed over a free-wheeling, unheated steel backup roll 25.4 cm (10 inches) in diameter where a 10.2 cm (4 inch) wide strip of the prepolymer syrup, which was delivered to the precision coating die using a Zenith Pump (available 20 from Zenith Corp.), was coated onto the first surface of the first substrate using a 10.2 cm (4 inch) die with no vacuum applied to the vacuum chamber. In Example 1 a coating die similar to that illustrated in Figure 6 was configured with a 0.51 mm (20 mil) shim, a 25 0° convergence, an overbite of 0.076 mm (3 mil), a coating land L_1 of 12.7 mm, a vacuum land 82 of 12.7 mm, and a die attack angle A_2 of 90°. In Example 2 a 20.3 cm (8 inch) wide strip of the prepolymer syrup was coated onto the first surface of the first substrate 30 using a 20.3 cm (8 inch) die similar to that used for Example 1 except that it was configured with a 0.48 mm (19 mil) shim and an overbite of 0.254 mm (10 mil). The coating gap was adjusted as indicated in Table 1

WO 97/10103

PCT/US96/13177

-14-

along with the pump speed and web speed to produce the coatings. No vacuum was applied to the vacuum chamber during the coating operation.

After the coating was applied to the first
5 substrate in each example, the second substrate was unwound from a second unwind roll and passed around a 2.54 cm (1 inch) diameter sintered metal laminator bar where it was laminated to the coated face of the first substrate according to the procedure described in the
10 aforementioned Vesley et al. application. The laminator bar was located approximately 12 cm (4.7 inches) downstream from the backup roll such that the coated web was not in contact with the backup roll or other idler or takeup roll at the point of lamination, and positioned so that the uncoated first substrate was
15 depressed approximately 3.8 mm (150 mils) below the plane defined by the first substrate as it passed between the backup roll and the idler roll; the extent of depression is hereinafter referred to as
20 "interference." Air pressure (approximately 2.1 bar) through the sintered metal bar was adjusted to provide a cushion of air between the laminator bar and the second substrate.

The thus produced uncured laminate construction
25 was cured to a high performance pressure sensitive adhesive by passing the construction under a bank of fluorescent black lights lamps (F20T12-350BL, available from Osram Sylvania, Danvers, MA). The laminate construction was exposed to 360 mJ/cm² of irradiation as
30 measured with a UVIRAD radiometer (model number UR365CH3, available from Electronic Instrumentation and Technology, Inc., Sterling, VA) equipped with a glass filter responsive between 300 and 400 nm, with a

WO 97/10103

PCT/US96/13177

-15-

maximum transmission at 365 nm. The average light intensity in the curing zone was about 2.3 mW/cm². Coating speeds were controlled by a vacuum pull roll positioned at the end of the coating line and were maintained at approximately 3.3 m/min. (11 feet/min).

Table 1 summarizes coating details for the two examples. The cured adhesive of example 2 adhered to the polyester when the laminated construction was peeled apart. Adhesive and shear properties of the cured polymer syrup of Example 2 were consistent with the properties obtained from similar formulations cured under the conditions described in U.S. Pat. No. 4,330,590.

Table 1

Ex.	First Substrate	Second Substrate	Viscosity (cps) ¹	Coating Cap (mm)	Coating Thickness (mm)
1	PET ²	PET ²	365	0.175	0.154±0.003
2	Release Paper ³	PET ²	5,600	0.127	0.150±0.001

- ¹ Measured on a Brookfield viscometer using a #4 spindle operating at 60 rpm
² Biaxially oriented PET film, 51 microns (2 mils) thick
³ Polyethylene-coated paper provided with a silicone release coating

Example 3

A PDLC device was prepared from a fluid containing (a) 55 parts of a mixture consisting of 30.0 wt.% RCC-15C curable matrix mixture obtained without initiator and with 50% less thiol (W.R. Grace, Atlanta, GA), 7.5 wt.% acrylic acid, 30.0 wt.% isooctyl acrylate, 15.0 wt.% 2-phenoxyethyl acrylate (Sartomer, West Chester, PA), 15.0 wt.% divinyl ether of triethylene glycol (International Specialty Products, Wayne, NJ), and 2.5 wt.% KB-1 photoinitiator, and (b) 45 parts BL036 liquid crystal mixture (EM Industries, Hawthorne, NY) having a

WO 97/10103

PCT/US96/13177

-16-

solution viscosity of 42 cps (measured on a Brookfield viscometer using a #3 spindle operating at 60 rpm). The fluid, which was degassed under vacuum for approximately 2 minutes at ambient temperature, was

5 applied as a 15.2 cm (6 inch) wide strip to the electrode surface of an ITO-coated polyester film (90/10 indium/tin ratio, 80 ohms/square, 51 microns (2 mil) thick PET, available from Southwall Technologies, Palo Alto, CA) at a rate of approximately 152.4 cm/min

10 (5 ft/minute) using the precision coating process described in Examples 1-2 except that a 88.9 cm die similar to that illustrated in Figure 7 was used. This die was deckled to produce a narrower coating and configured with a 152 micron shim, a coating land

15 having a length (L_1) of 12.7 mm, a vacuum land having a length L_2 of 12.7 mm, a 0.57° convergence, a 33 micron overbite, a vacuum land gap G_2 of 0.152 mm, a die attack angle A_2 of 95° , and a coating gap of 102 microns. The convergence of the vacuum bar was 0° and no vacuum was

20 applied to the vacuum chamber during coating. Both the die and back-up roll were temperature controlled at 21°C . A pressure of 1.7 bar was maintained to the sintered metal bar during lamination and the lamination bar was adjusted to provide an interference of 3.6 mm.

25 The uncured laminate construction was cured by passing the construction through a cooled curing chamber constructed of ultraviolet transparent Acrylite™ OP-4 (available from Cyro Industries, Mt. Arlington, NJ), extending approximately 61 cm (2 feet)

30 into a cure chamber equipped with two banks of fluorescent black lights (F20T12-350BL, available from Osram Sylvania, Danvers, MA), one bank positioned on each side of the laminate. Air temperature in the

WO 97/10103

PCT/US96/13177

-17-

cooling chamber was monitored by a thermocouple mounted in the chamber under the second fluorescent bulb and controlled at the indicated temperature by introducing temperature controlled air. Each side of the laminate construction was exposed to approximately 530 mJ/cm² of radiation calculated from light intensities of 1.1 mW/cm² as measured through the conductive electrode used in the PDLC device by means of a UVIBRITE radiometer (model number UBM365MO, available from Electronic Instrumentation and Technology, Inc., Sterling, VA) equipped with a glass filter responsive between 300 and 400 nm, with a maximum transmission at 365 nm. The radiometer was specially calibrated to read in absolute intensity.

The backup roll 50 was a pacer roll driven by a Torquer Tachometer precision motor (available from Inland Motor Division, Bradford, VA).

The cured coating thickness of the resulting PDLC film was 24±1 microns. The PDLC device had on- and off-state transmissions of 73.1% and 1.2%, respectively, and a haze of 5.8%.

Example 4

A PDLC device was prepared as described in Example 3 except that a fluid containing (a) 57.5 parts of a mixture consisting of 13.7 wt.% lauryl methacrylate (Rhom Tech, Inc., Malden, MA), 3.9 wt.% methacrylic acid (Aldrich, Milwaukee, WI), 80.4 wt.% RCC-15C prepared without initiator (W.R. Grace, Atlanta, GA), and 2 wt.% photoinitiator KB-1, and (b) 42.5 parts of BL036 liquid crystal mixture, with a solution viscosity of 210 cps (measured on a Brookfield viscometer using a #4 spindle operating at 60 rpm), was used. The die was configured with a 152 microns shim having a slot width

WO 97/10103

PCT/US96/13177

-18-

of 88.9 cm, a 76 micron coating gap, and a 51 micron overbite. The coating was applied as a 88.9 cm wide strip of the uncured matrix on the ITO coated PET film at a web speed of 0.91 m/minute (3 feet/minute).

5 During coating, a 3.7 mm Hg (2 inches water) vacuum was applied to the vacuum chamber. During lamination, an interference of 3.8 mm was used. The laminate construction was exposed to 330 mJ/cm² of UV light having an average intensity of 1.7 mW/cm².

10 The thickness of the cured coating was 21±0.6 microns. The PDLC device had on- and off-state transmissions of 74% and 2.7%, respectively, and a haze of 4.5% .

Example 5

15 A PDLC device was prepared as described in Example 4 except that the fluid contained 500 parts of BL036 liquid crystal mixture and 333 parts of a mixture having the composition of 2.5 wt.% Esacure KB-1 photoinitiator, 7.5 wt.% acrylic acid, 30.0 wt.%
20 isooctyl acrylate, 15.0 wt.% 2-phenoxyethyl acrylate, 15.0 wt.% Uralac 3004-102 (DSM Resins, U.S., Inc., Elgin, IL), and 30.0 wt.% Uralac 3004-300 (DSM Resins, U.S., Inc., Elgin, IL). The die was configured with an overbite of 43 microns, a vacuum land gap G₂ of 24.5 mm
25 and a vacuum of 1.9 mm Hg was applied to the vacuum chamber during coating. The ITO-coated polyester film used for the electrodes was approximately 130 microns (5 mils) thick. An air pressure of 3.4 bar was maintained to the laminator bar which was adjusted to
30 provide an interference of 6.35 mm. The resulting laminate was exposed UV light having an average intensity of approximately 1.68 mW/cm² at about 23°C to produce a PDLC film approximately 18 microns thick.

WO 97/10103

PCT/US96/13177

-19-

The PDLC device had on- and off-state transmissions of 73.4% and 1.7%, respectively, and a haze of 5.3%.

Example 6

5 A PDLC device was prepared as described in Example
4 except that a fluid containing (a) 45 parts of a
mixture consisting of 2.5 wt.% KB-1 photoinitiator,
20.0 wt.% 9460 allyl aliphatic urethane (Monomer
Polymer & Dajac, Trevose, PA), 35.0 wt.% isooctyl
10 acrylate, 7.5 wt.% acrylic acid, 20 wt.% 2-phenoxyethyl
acrylate, and 15.0 wt.% Uralac 3004-102, and (b) 55
parts of BL036 liquid crystal mixture, with a solution
viscosity of 64 cps (measured on a Brookfield
viscometer using a #3 spindle operating at 60 rpm), was
15 used. The die was configured with a 152 micron shim
having a slot width of 88.9 cm, an overbite of 30
microns and the coating applied to the ITO coated PET
substrate at a rate of 3 m/min. at 20°C with a vacuum of
2.8 mm Hg applied to the vacuum chamber. An air
20 pressure of 3.4 bar was maintained to the lamination
bar which was adjusted to provide an interference of
3.8 mm. The laminate construction was exposed to 303
mJ/cm² of UV light having an average intensity of 1.6
mW/cm².

25 The cured coating thickness was 17.4±0.6 microns.
The PDLC device had on- and off-state transmissions of
70.0% and 0.8%, respectively, and a haze of 8.6%.

Example 7

30 A syrup consisting of 98 wt.% isooctyl acrylate, 2
wt.% acrylic acid, and 0.04 wt.% Esacure KB-1 was
polymerized as described in U.S. Pat. No. 4,330,590
(Vesley) to a viscosity of 3,000 cps (measured on a
Brookfield viscometer using a #4 spindle operating at

WO 97/10103

PCT/US96/13177

-20-

60 rpm). An additional 0.1 wt.% KB-1 and 0.2 wt.% hexanediol diacrylate was added to the partially polymerized syrup and the syrup was coated according to the procedure described in Example 1 except that a 20.3
5 cm (8 inch) die having a 76 micron coating gap, a 50.8 micron shim, a 76 micron overbite and a 0° convergence was used to coat a 14 cm (5.5 inch) wide, 0.051 mm thick strip of the uncured syrup onto a 0.051 mm thick biaxially oriented PET film which had previously been
10 coated with a silicone release coating.

A second syrup having a composition of 85 wt.% isooctyl acrylate, 15 wt.% acrylic acid and 0.04 wt.% KB-1 was photopolymerized to a viscosity of approximately 5000 cps (measured on a Brookfield
15 viscometer using a #4 spindle operating at 60 rpm) according to the procedure described above in preparing the first syrup. An additional 0.1 wt.% KB-1 and 0.2 wt.% hexanediol diacrylate was added to the partially polymerized syrup and an approximately 0.65 mm thick
20 coating of the second syrup was notched bar-coated onto the release coated surface of a second 0.51 mm thick PET film. The two unpolymerized films were laminated together using a 2.54 mm interference setting. The resulting laminate was cured as in Example 1 to form a
25 pressure sensitive adhesive film having a total thickness of 0.72 ± 0.03 mm which displayed differential adhesion.

Example 8

A PDLC device was prepared from a fluid containing
30 (a) 45 parts of a mixture consisting of 80.4 wt.% RCC-15C curable matrix mixture obtained without initiator, 17.6 wt.% isooctyl acrylate, and 2.0 wt.% KB-1 photoinitiator, and (b) 55 parts BL036 liquid

WO 97/10103

PCT/US96/13177

-21-

crystal mixture having a solution viscosity of 210 cps (measured on a Brookfield viscometer using a #4 spindle operating at 60 rpm). The fluid was applied as a 10.2 cm wide strip to the electrode surface of an ITO-coated polyester film at a rate of approximately 1.5 m/minute at 21°C as described in Example 1. The coating die was configured with a 152 micron shim, a 0.57° convergence, an overbite of 25.4 micron, and a coating gap of 102 micron. A vacuum of 3.7 mm Hg was applied to the vacuum chamber of the die during coating. The lamination roll was a 6.35 cm diameter idler roll which was positioned to provide an interference of 3.9 mm. The exposure during cure was 322 mJ/cm² and the average light intensity was 1.5 mW/cm².

The cured coating thickness was 20.0 microns. The PDLC device had on- and off-state transmissions of 72% and 0.2%, respectively, and a haze of 7.2%.

Other embodiments are within the following claims.

For example, instead of depressing lamination bar 30 (around which substrate 26 passes) in order to laminate substrates 12 and 26 together, lamination bar 30 can be held stationary, and one or both of rolls 18 and 22 moved to laminate the two substrates together in lamination zone L.

WO 97/10103

PCT/US96/13177

-22-

WHAT IS CLAIMED IS:

1. A method of preparing a laminate comprising the steps of:

5 introducing a first substrate having first and second surfaces and supported at two or more points into a lamination zone located between two of the support points,
said first substrate being unsupported throughout said lamination zone;
10 introducing a second substrate having first and second surfaces into said lamination zone such that said first surfaces of said substrates are in a facing relationship with each other in said lamination zone,
at least one of said first surfaces being provided
15 with a coating; and
moving said substrates relative to each other to laminate said second substrate to said first substrate in said lamination zone.

2. The method of claim 1 comprising passing said
20 second substrate around a lamination bar to position said first surfaces of said substrates in a facing relationship with each other in said lamination zone; and

depressing said lamination bar to laminate said
25 second substrate to said first substrate in said lamination zone.

3. The method of claim 1 comprising moving at least one of said support points supporting said first substrate to laminate said second substrate to said
30 first substrate in said lamination zone.

WO 97/10103

PCT/US96/13177

1/5

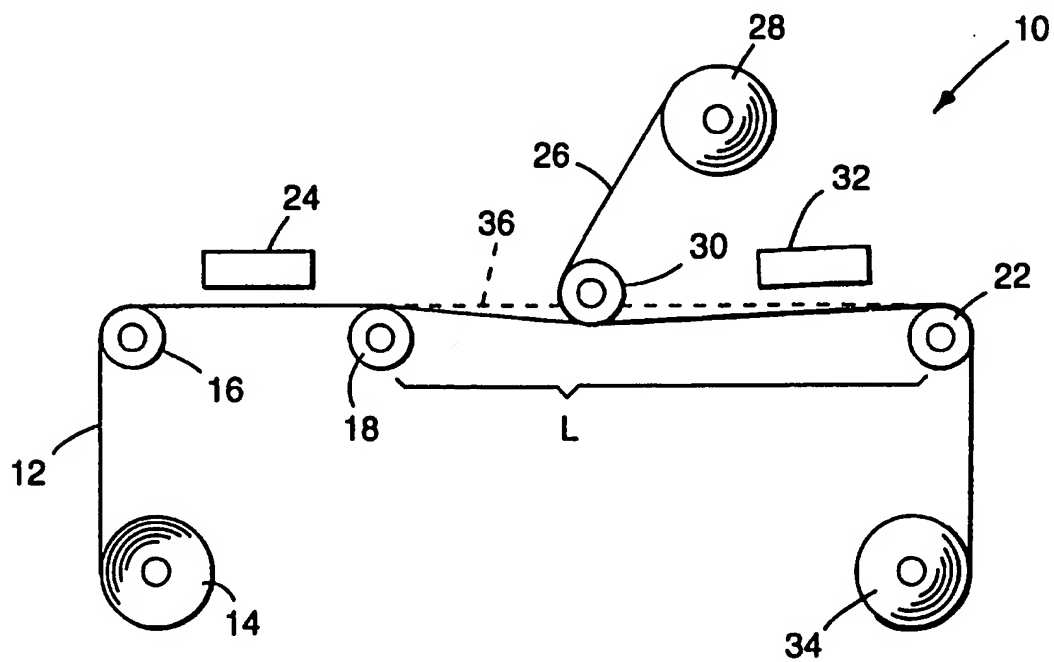


FIG. 1

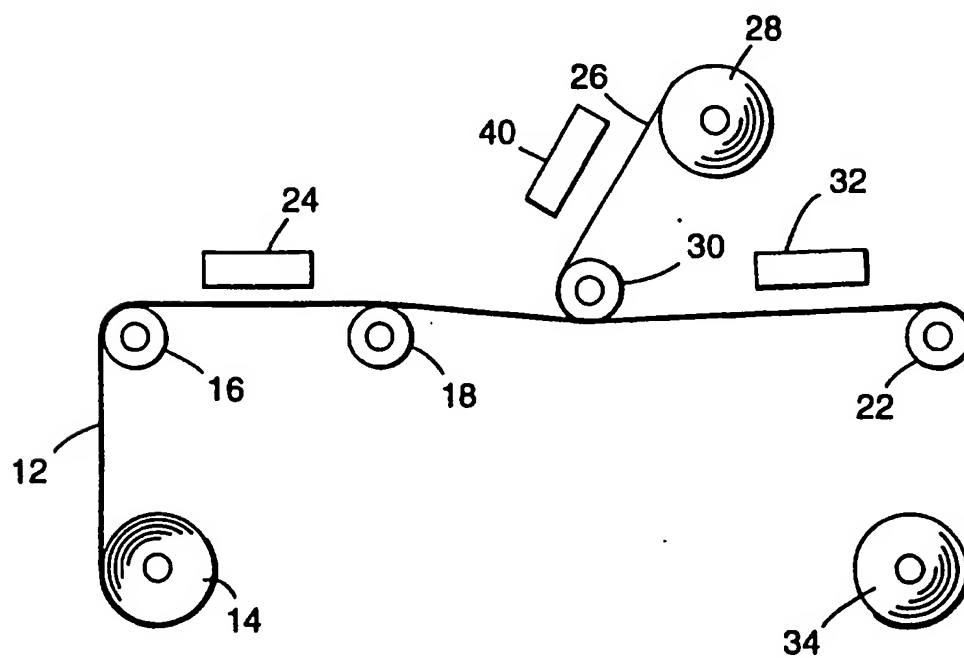


FIG. 2

WO 97/10103

PCT/US96/13177

2/5

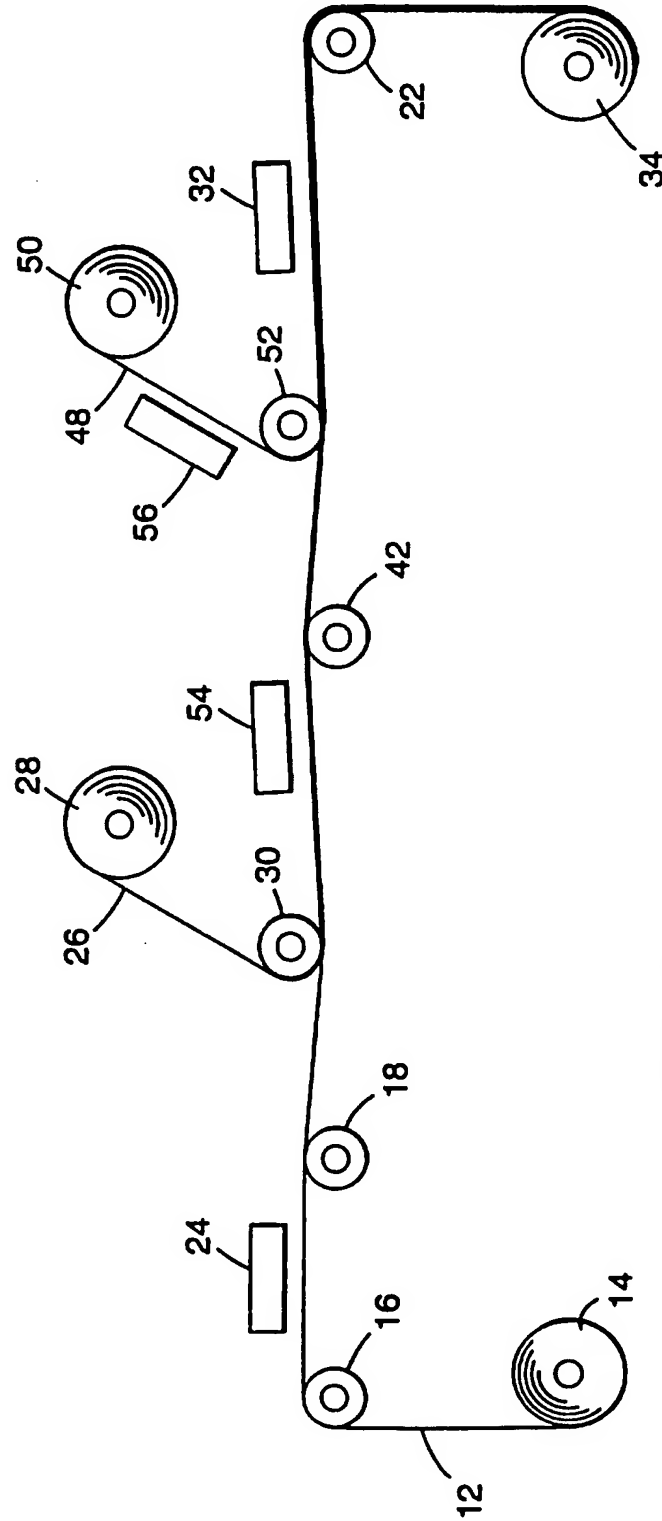


FIG. 3

WO 97/10103

PCT/US96/13177

3/5

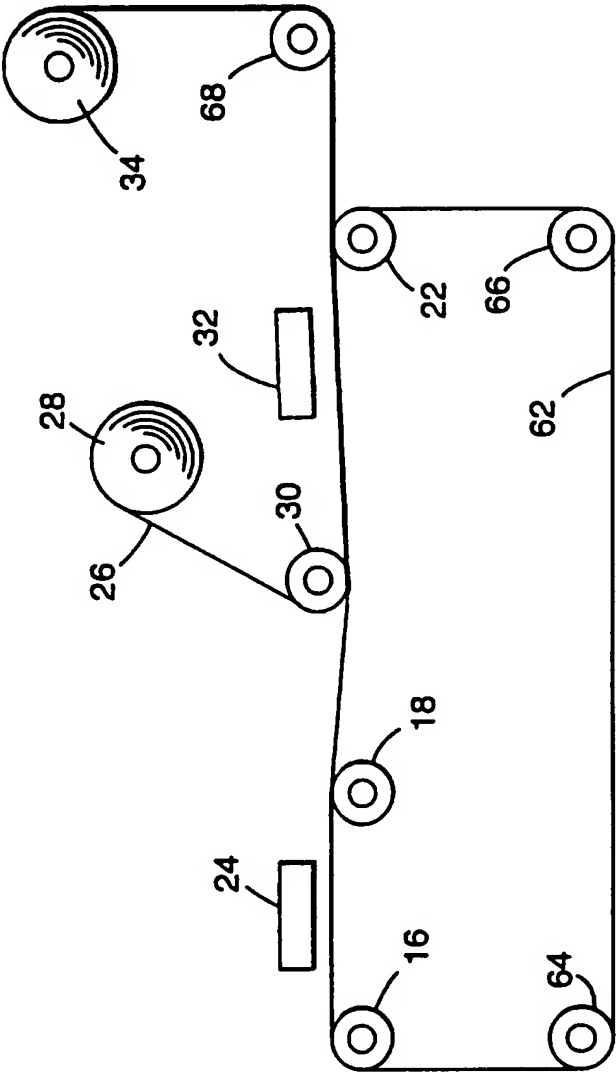
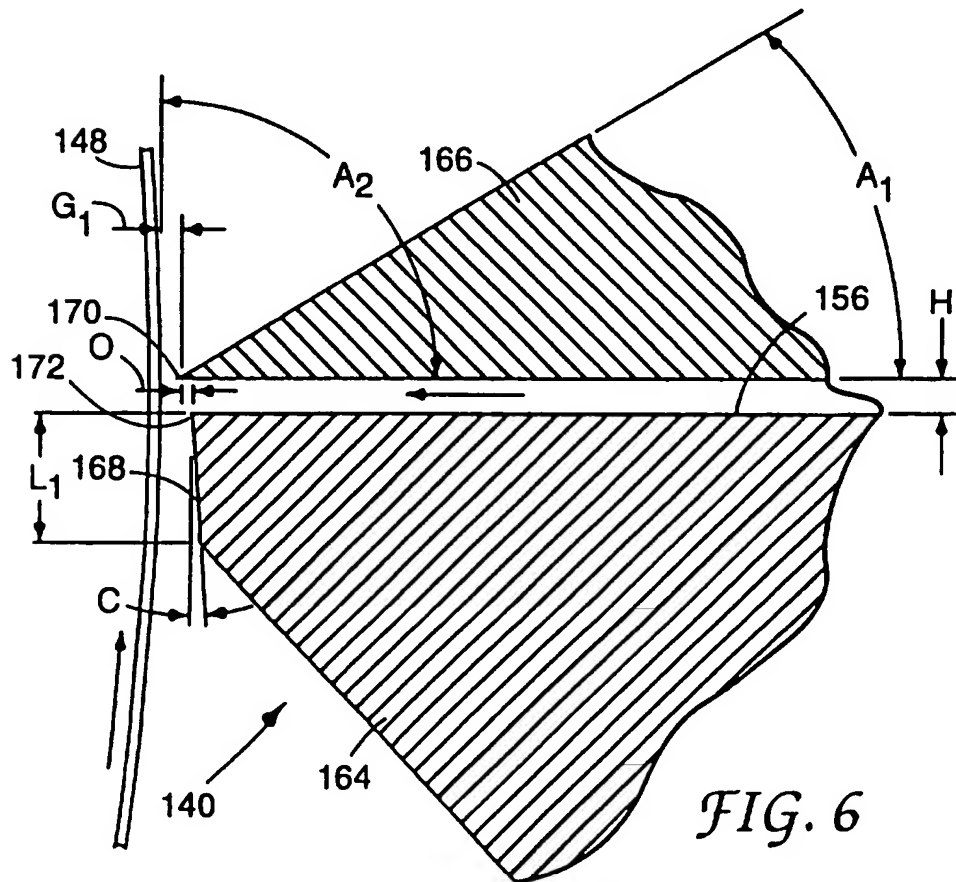
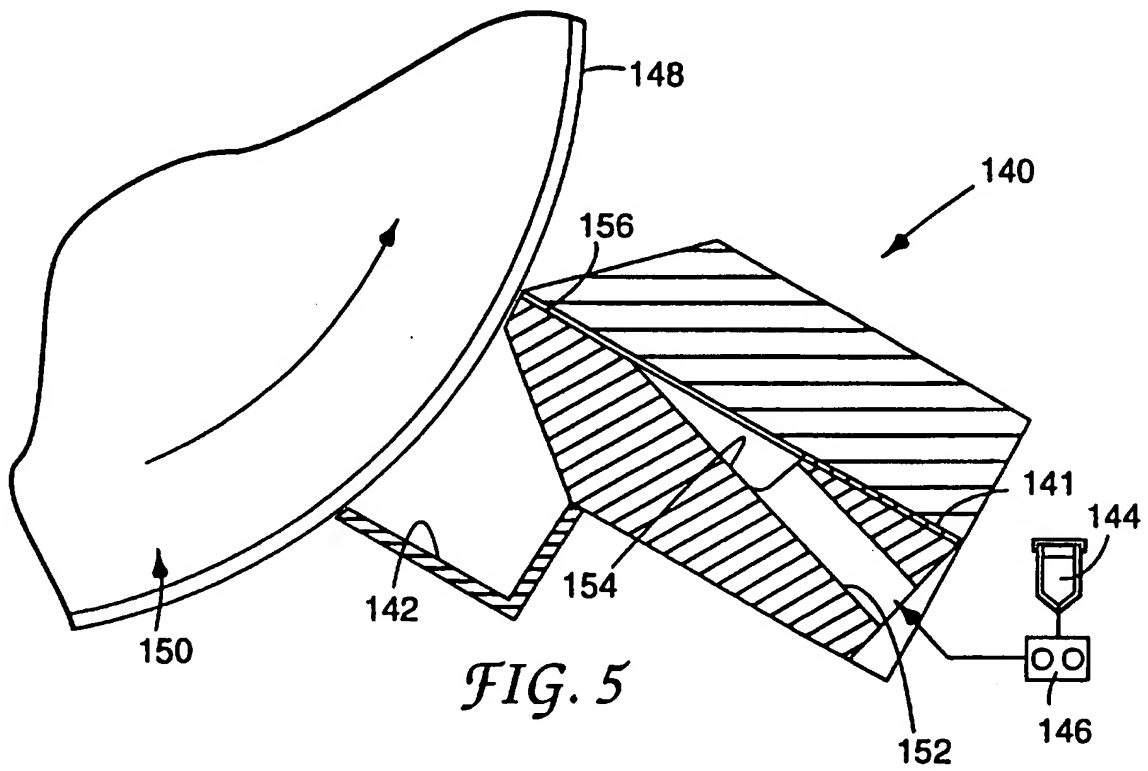


FIG.4

WO 97/10103

PCT/US96/13177

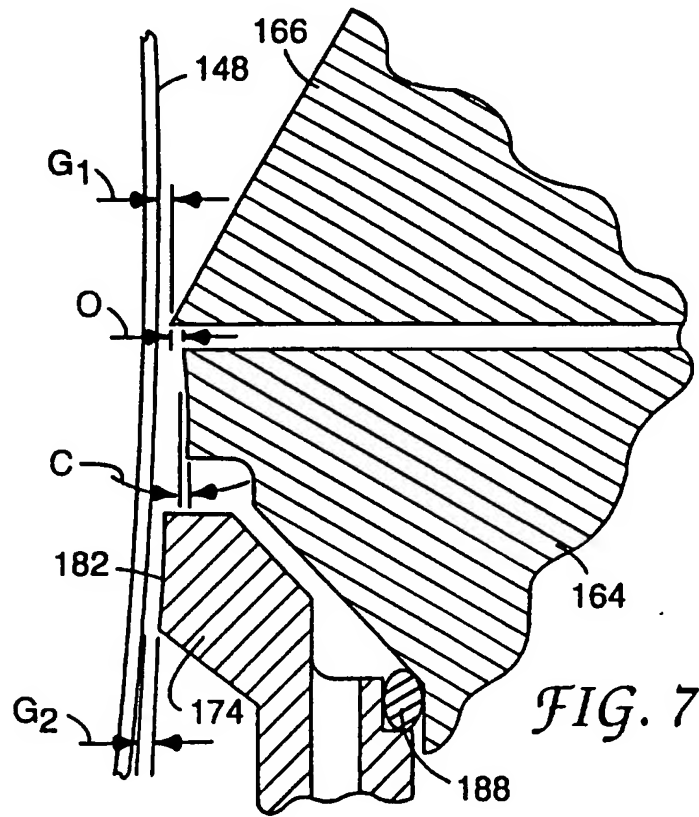
4/5



WO 97/10103

PCT/US96/13177

5/5



INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/US 96/13177

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B32B31/06		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 6 B32B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X, L	WO,A,95 29811 (MINNESOTA MINING & MFG) 9 November 1995 see the whole document ---	1-3
X	EP,A,0 236 616 (ENERGY SCIENCES INC) 16 September 1987 see column 3, line 20 - column 4, line 11 see abstract; figures ---	1,2
A	EP,A,0 616 880 (IDEMITSU PETROCHEMICAL CO) 28 September 1994 see abstract; figures ---	1-3
A	US,A,2 667 436 (GOEPFERT) 26 January 1954 see column 3, line 57 - column 4, line 35 see figures 4,5 -----	1-3
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art '*&' document member of the same patent family		
Date of the actual completion of the international search 18 November 1996		Date of mailing of the international search report 02.12.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Lanaspeze, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/13177

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9529811	09-11-95	NONE	
EP-A-0236616	16-09-87	US-A- 4642244 JP-A- 62210072	10-02-87 16-09-87
EP-A-0616880	28-09-94	JP-A- 6246829 CA-A- 2116290	06-09-94 26-08-94
US-A-2667436	26-01-54	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.